



Advanced Concepts for Containment of Hydrogen and Hydrogen Storage Materials

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**Project ID #
ST16**

This presentation does not contain any proprietary or confidential information

Overview



Timeline

- Start date: **October 2003**
- End date: **September 2008**
- Percent complete: **30%**

Budget

- Funding received in FY04: **\$500 k**
- Funding for FY05: **\$625 k**
- SCAQMD funding: **\$500 k**

Barriers

- **B. Weight and volume**
- **D. Durability**
- **E. Refueling Time**
- **H. Sufficient fuel storage for acceptable vehicle range**
- **I. Materials**
- **K. Balance of plant (BOP) components**
- **M. Hydrogen capacity and reversibility**

Partners

- Demonstrating cryotank technology (**SCI, SunLine**, funded by **SCAQMD**)
- Working with **BMW** on cryo storage
- **Spencer composites**, CRADA with **Automotive Composites Consortium**, aerospace work funded by **DARPA**
- Collaboration with many **Universities**

Objectives: We are developing high performance conformable containers that can operate under extreme conditions, as needed for hydrogen and hydrogen storage material containment



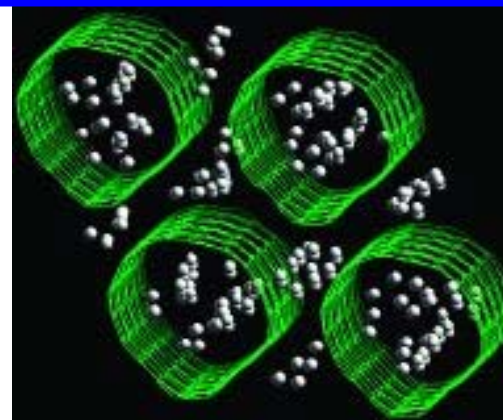
Liquid: develop conformable containers that can operate at extremely low temperature (20 K) and wide range of pressures (100-5000 psi)



Compressed: develop containers for very high pressure (10,000 psi) and moderate temperature (up to 100°C)

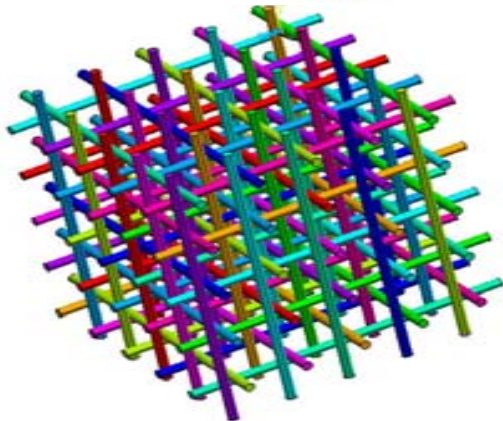
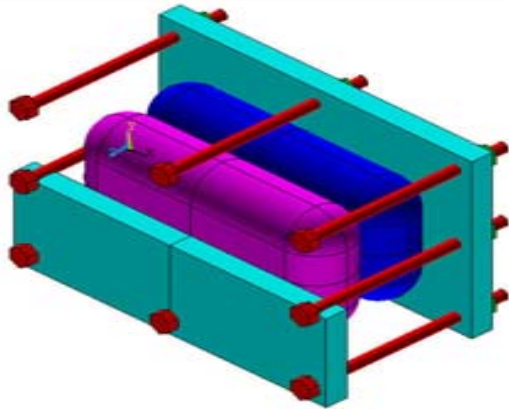


Chemisorbed: develop conformable containers for high temperature operation and efficient thermal management

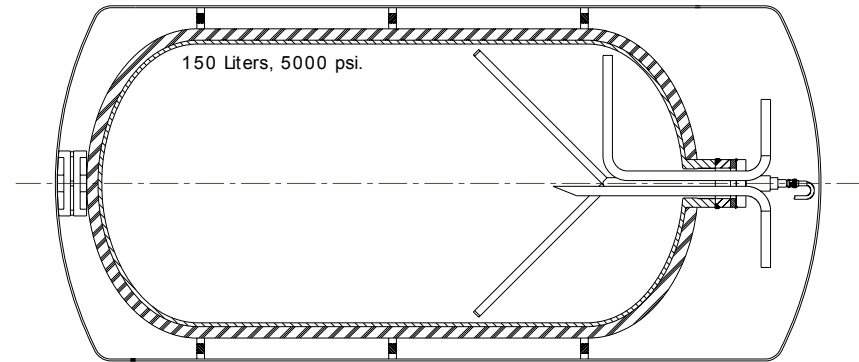


Physisorbed: develop compact containers that operate over wide range of conditions and provide efficient thermal management

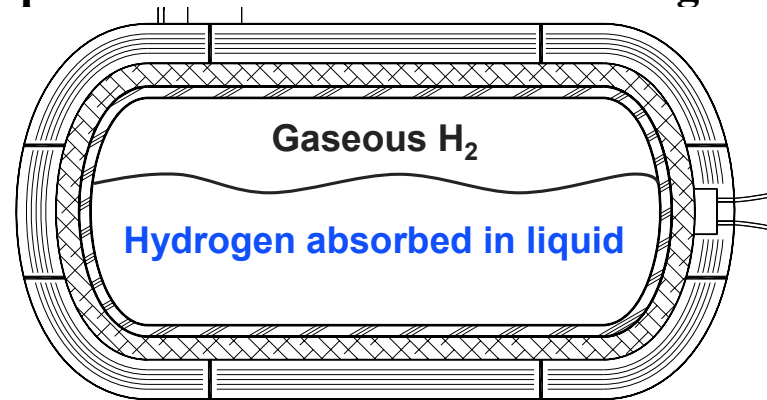
Approach: we are developing innovative concepts for hydrogen and hydrogen storage material containment for efficient thermal management at cryogenic or high temperatures



Conformable containers efficiently use available space in the vehicle. **Ribs and struts** provide heat transfer paths for efficient thermal management

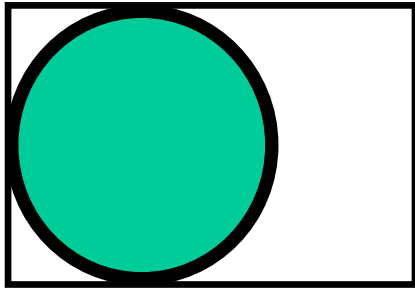


Insulated pressure vessels are needed for cryogenic operation with low evaporative losses. **Supercritical hydrogen** ($p \sim 5000$ psi, $T \leq 50$ K) has the potential to meet the 2015 DOE goals

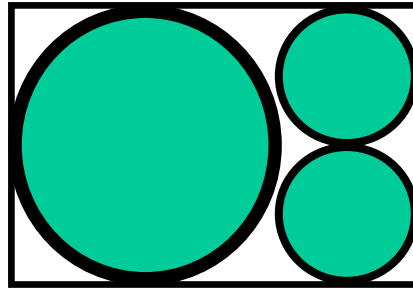


Hydrogen absorbed in liquid nitrogen is safe, easy to dispense, light and compact

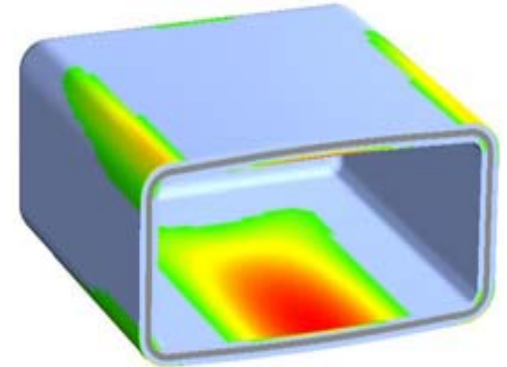
Accomplishments: We have analyzed multiple geometries for continuous fiber conformable containers and selected an optimum design



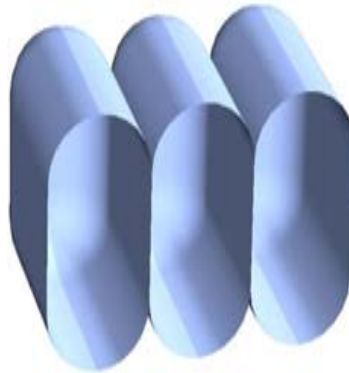
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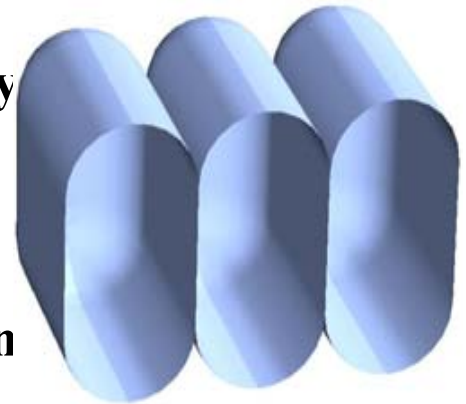
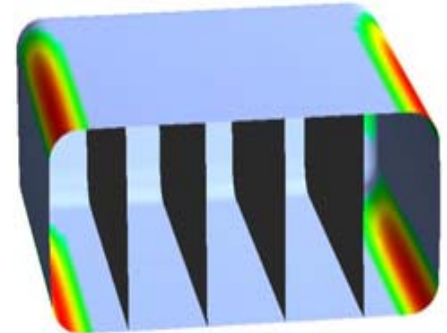
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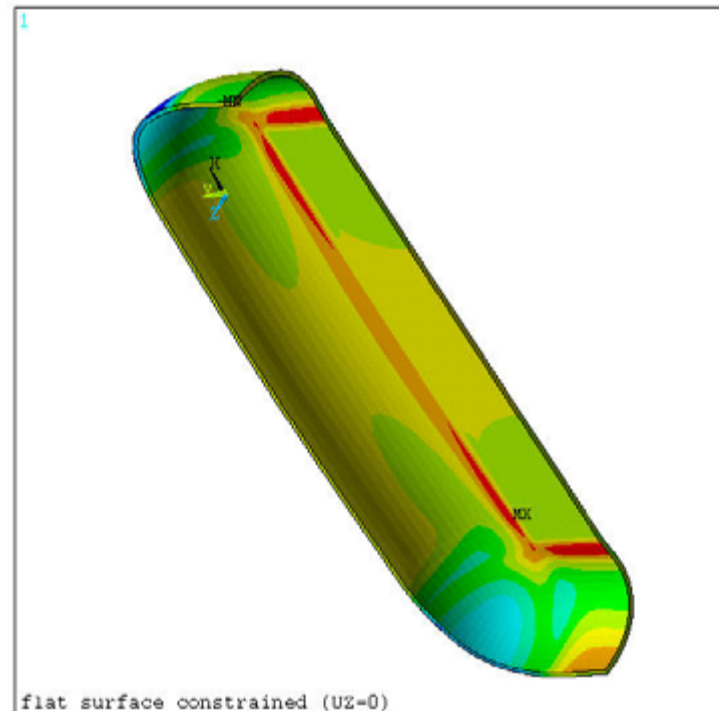


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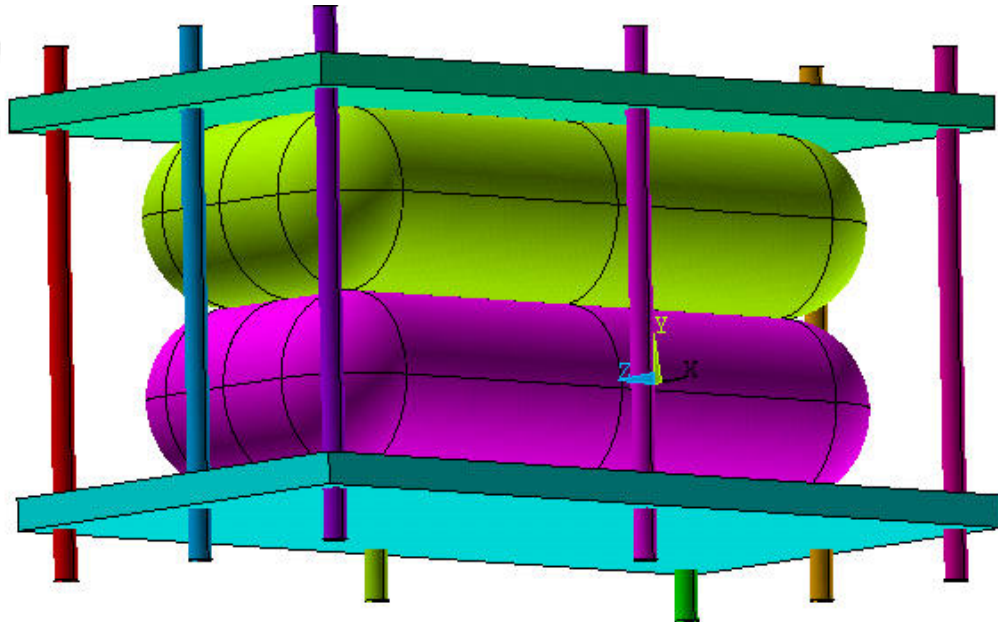
- Conformable vessels can improve the volumetric efficiency of hydrogen containers
- Determined optimum geometry and conducted extensive finite element analysis
- Colors in figures indicate regions with stress concentration

We have determined an optimum design for continuous fiber conformable containers and we are moving toward experimental testing of small scale components



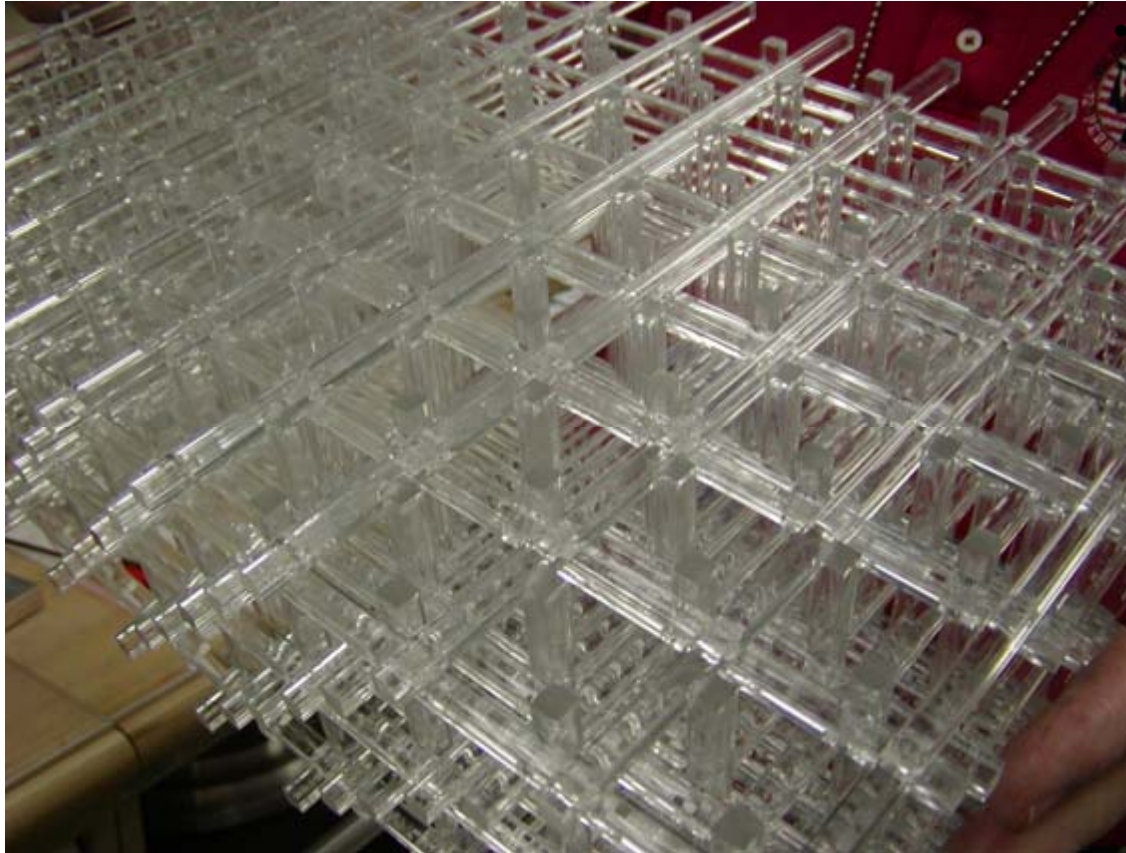
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155201
168204



- Have conducted extensive finite element analysis of our vessel design
- In the process of building small scale vessels (10 cm long) for component testing
- Steel plates simulate series of segments
- To be tested in high pressure lab

We have produced the first manufacturable macrolattice structure for conformable pressure vessels



• **Appears cubic**

- **Actually C3i**

Reduced
Symmetry

Struts pass each
other, avoid any
nodes

- **Only 2 struts pass
close to one
another at any
point (not 3)**

Weak glue bonds

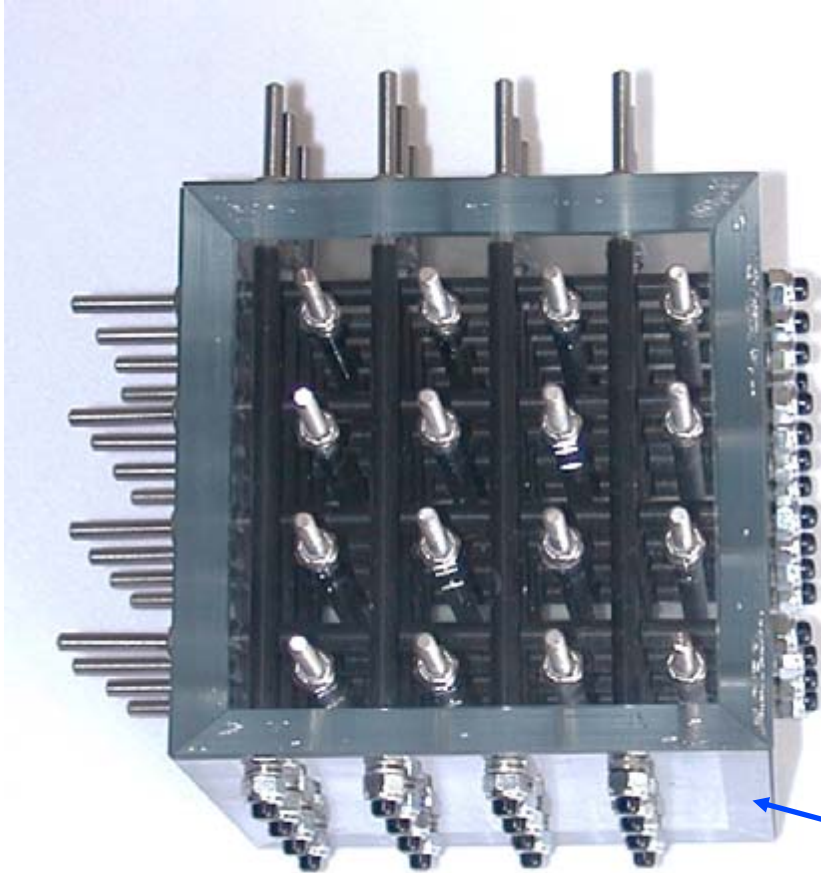
‘Stitched’ together
by robot bonder

Bond corridors

- **Model has correct volume fraction for best composite structure**

Area ratio 1/18 on each axis (or 1/6th struts by volume) was designed for
22,000 psi burst with uniaxial struts that are built to fail at 400,000 psi

We have built a generation zero prototype (functional model that can be pressurized) of a macrolattice pressure vessel



**Custom Neoprene Gasket is
bonded to join 12 edges at
8 corners**

Polycarbonate skin faces (6 identical)

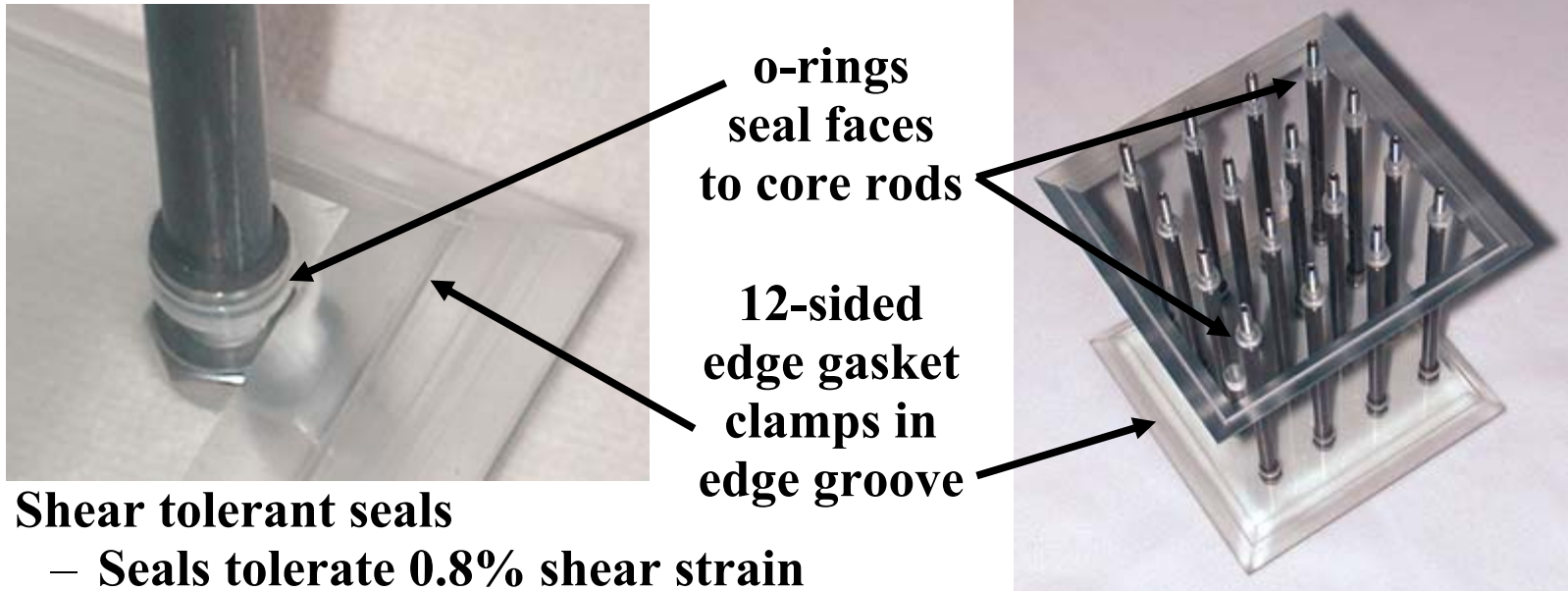
- **Design and construction completed**
- **Vessel has high volumetric efficiency (projected 84%)**
- **Extensively analyzed by finite element**

Our second generation zero prototype is capable of resisting pressure



and it has hollow struts for improved thermal management

- **Seals added in second prototype**
 - Details include piston-like o-ring seal between core rods and faces (rigid in bending) which can tolerate 0.035" expansion to mimic composite strain; and edge seal backing groove to tolerate very high proof pressures (to qualify prototype at 5:1 SF)

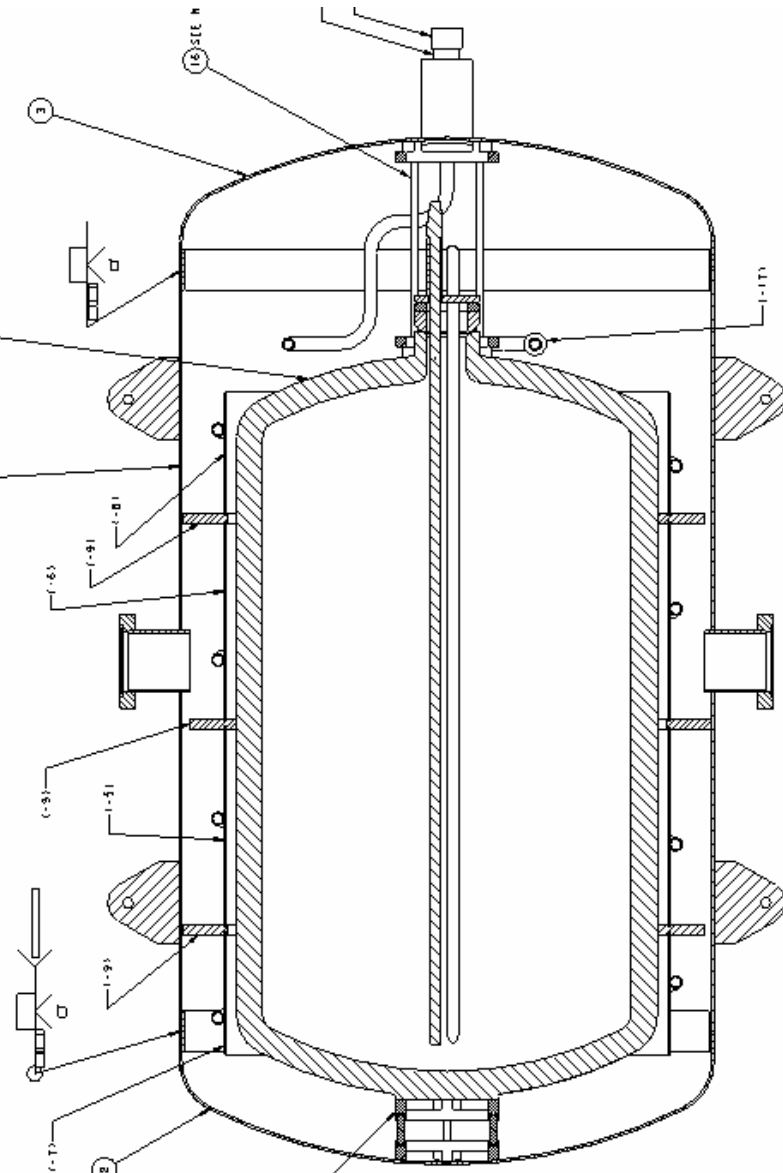


- **Shear tolerant seals**
 - Seals tolerate 0.8% shear strain
 - Much lower shear stiffness vs. axial stiffness (100:1) enables demo of major safety feature = content retention while warped



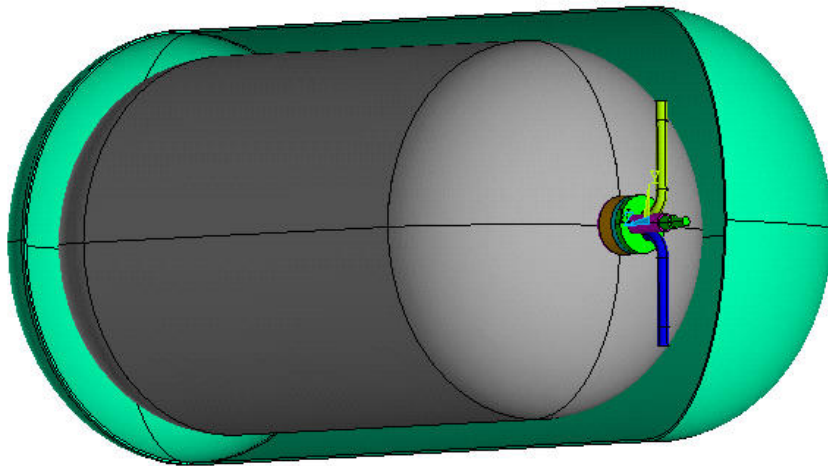
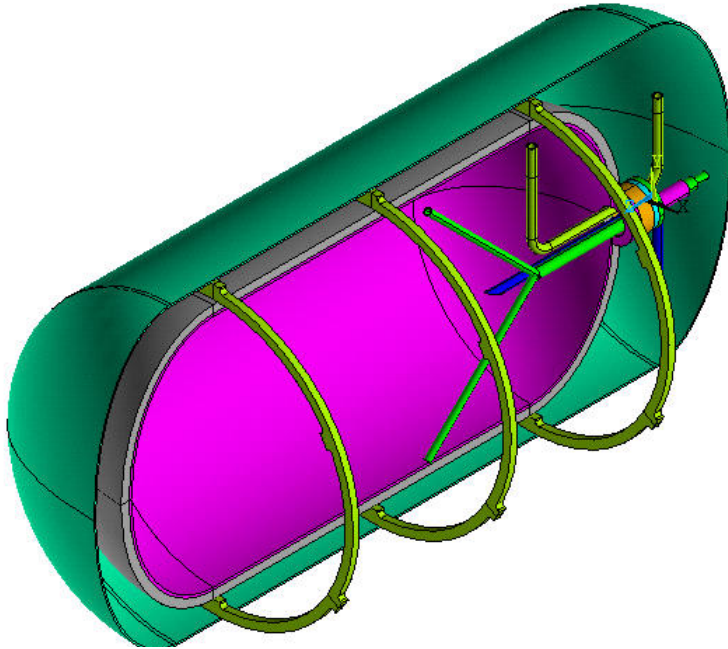
- **Tubing replaces solid core rods to demo heat exchange**

Our first generation insulated pressure vessel has demonstrated the possibility of flexible refueling and operation with liquid and compressed hydrogen



- **Fueling with CH_2 for lower energy consumption (75% less storage energy vs. LH_2)**
- **2X-3X longer range with LH_2**
- **Successfully conducted proof of concept experiment in SunLine pickup truck (funded by SCAQMD)**
- **Meets 2005 DOE weight goal**
- **1.67 kWh/kg, 0.77 kWh/L, 3600 psi**
- **Works in the vertical position**
- **Can be used for storage materials (cryogenic carbon)**
- **Wrote set of certification standards (funded by AQMD)**

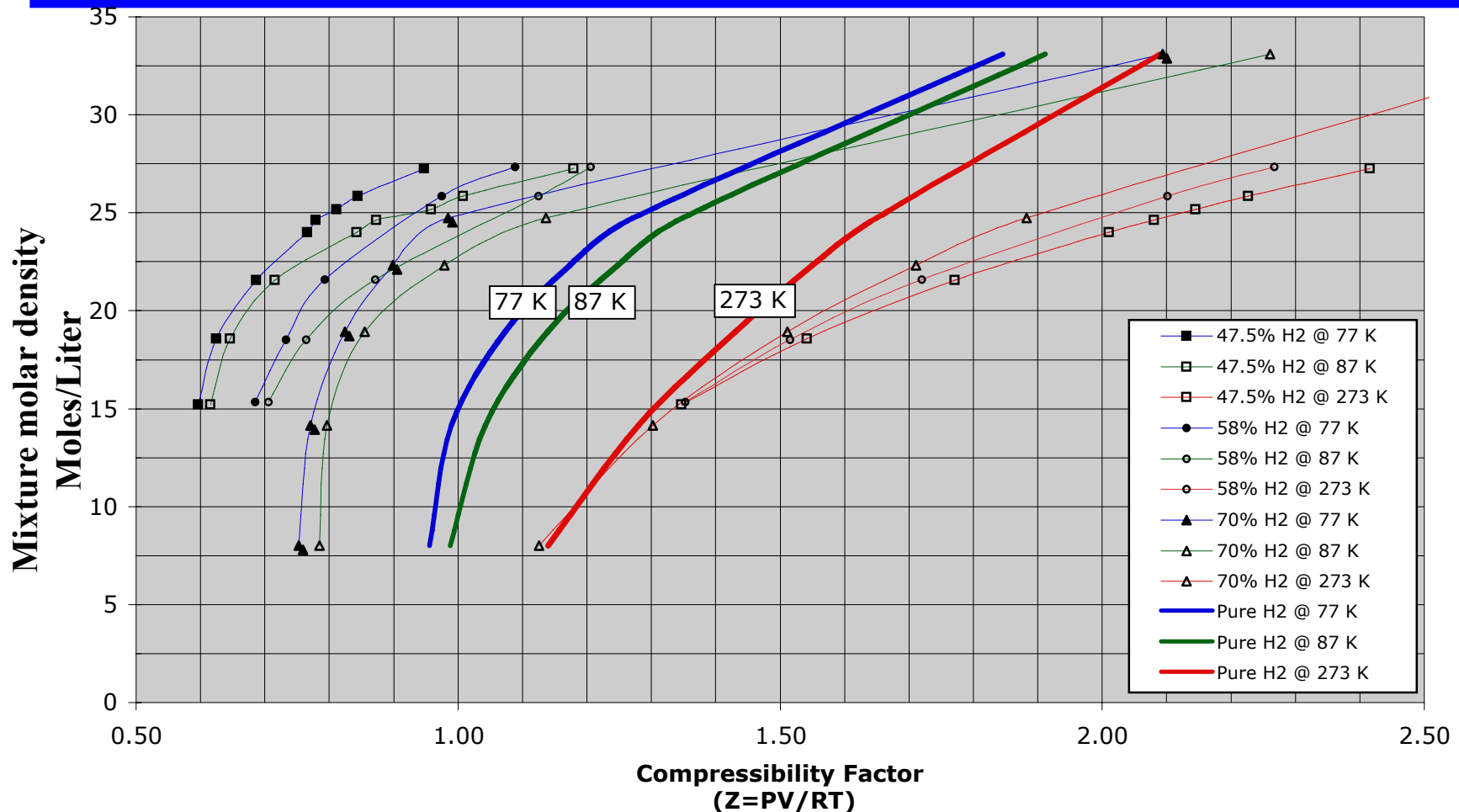
Our second generation insulated pressure vessel has much improved volume, weight and operational performance with respect to previous design



- **Much improved performance**
- **Meets 2010 DOE weight and 2005 volume goals**
- **2.32 kWh/kg, 1.22 kWh/L, 5000 psi**
- **Works in the horizontal position**
- **Fits across the bed of a compact pickup truck or inside the trunk of a midsize car**
- **Projected to virtually eliminate evaporative losses**
- **Very good liquid hydrogen tank**
- **To be tested in collaboration with BMW**

We have characterized hydrogen absorption in liquid nitrogen with anticipated refuelability and safety advantages

Our results indicate favorable absorption of H₂ into LN₂

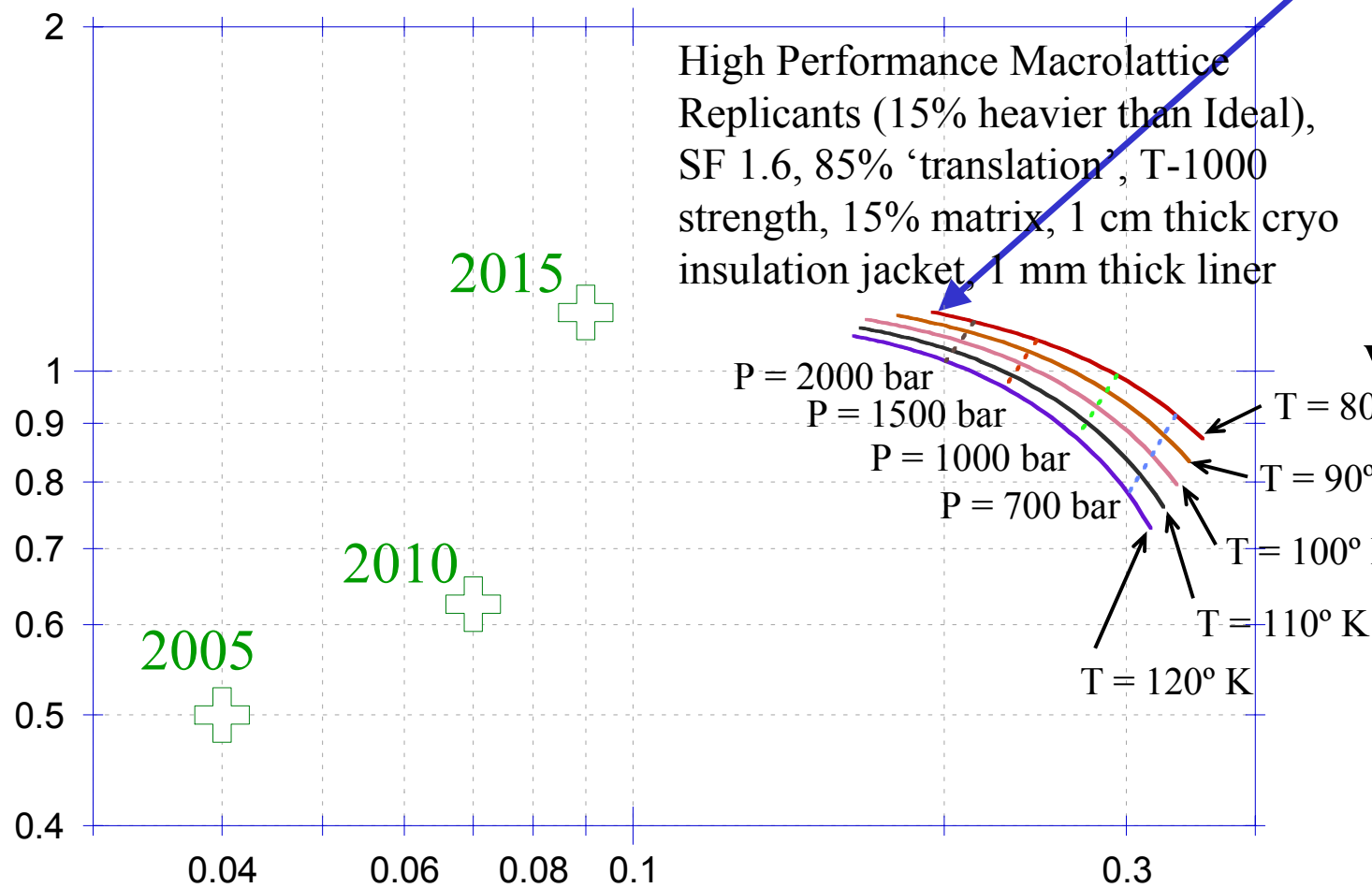


Thick lines are for pure hydrogen and thin lines are for mixtures of hydrogen and nitrogen. At ice temperature (273 K), the compressibility factor (and therefore the volume) is higher for the mixture than for the pure H₂ because no absorption occurs. At LN₂ temperatures, considerable absorption occurs, and the mixtures are more compact than the pure H₂

We have examined the entire phase diagram for hydrogen and we have identified supercritical hydrogen (80 K, 1000 bar) as a promising operating point for meeting the 2015 goals



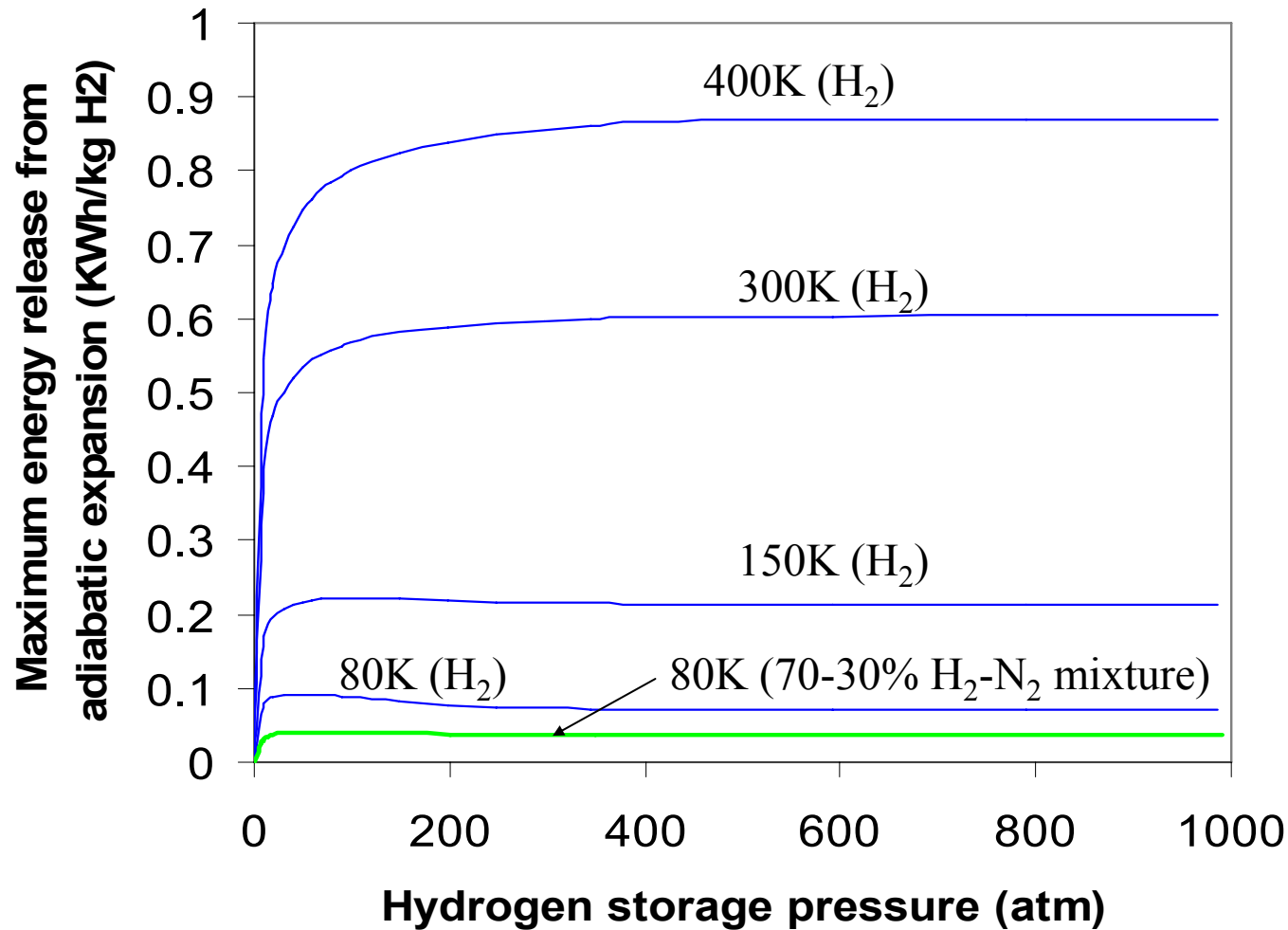
H₂ storage density / liquid H₂ density



Supercritical hydrogen has the potential of meeting the 2015 DOE weight and volume goals with future advanced pressure vessels

Hydrogen Fraction of Subsystem Mass (dimensionless)

Cooling hydrogen makes it safer: energy release during a sudden failure is a weak function of pressure but a strong function of temperature



Hydrogen absorbed in nitrogen has lower energy because the nitrogen is near the point of liquefaction. Once liquefied, the density of nitrogen is fairly constant and therefore it does not contribute to the expansion energy.

Summary of accomplishments: we have achieved considerable progress towards developing high performance containers for hydrogen and hydrogen storage materials



- Designed and built prototype **macrolattice** conformable vessels
- Analyzed and designed **continuous fiber** conformable container
- Installed **insulated pressure vessel** in pickup truck and demonstrated flexible refueling with liquid and compressed H₂
- Designed a new **insulated pressure vessel** that works in the horizontal position and meets the 2010 DOE weight goal and the 2005 DOE volume goal
- Characterized **absorption of hydrogen in nitrogen** at low temperatures with anticipated safety and delivery advantages
- Identified **supercritical hydrogen** as an operating condition that has potential for meeting the 2015 DOE goals
- **Wrote** 2 patents, 5 invited papers, 2 contributed papers, 1 technical report, 1 set of safety standards and to deliver 2 invited presentations

Responses to reviewers' comments:
We have refocused our project plans
to directly address the reviewers' comments



- *Would like to see more actual testing and see it earlier in the program.* We have developed prototypes for conformable vessels and insulated pressure vessels that will be tested this year.
- *Need to work with pressure vessel manufacturers.* We have worked with SCI for multiple years on cryogenic pressure vessels and with Thiokol/Quantum on lightweight vessels
- *It is difficult to see how the 2015 or even the 2010 targets can be met.* We are planning to meet the 2010 weight goal with our new insulated pressure vessel. The 2015 targets require the development of high performance tanks for supercritical operation
- *Compressed hydrogen is not the answer to on-board storage.* Our work is not limited to storage of compressed hydrogen. Our container designs are necessary for cryogenic H₂ and enable efficient thermal management of hydrogen storage materials



Analysis

- Continue conceptual analyses and begin detailed analyses
- Begin application analysis
- Analyze thermal management capability of macrolattice

Design

- Conclude conceptual design by creating CAD models of the elements
- Develop engineering requirements for macrolattice components
- Finalize design of second generation insulated pressure vessel

Building and Testing

- Pressure test newly built macrolattice conformable container
- Build and pressure test new insulated pressure vessel
- Build and pressure test continuous fiber conformable container
- Build and test new insulated pressure vessel (with BMW)



Supplemental slides

Publications and presentations



Patents

- **Lightweight Cryogenic-Compatible Pressure Vessels for Vehicular Fuel Storage**, Salvador M. Aceves, Gene Berry, Andrew H. Weisberg, US Patent 6,708,502 B1, March 23, 2004. World Patent WO 2004/029503 A2, April 8 2004.
- **Storage of H₂ by Absorption and/or Mixture within a Fluid**, Gene Berry and Salvador Aceves, World Patent WO 2005/015076 A1, February 24, 2005.

Publications in Books and Technical Journals

- **Hydrogen Storage and Transportation**, Gene Berry, Joel Martinez-Frias, Francisco Espinoza-Loza, Salvador Aceves, Invited chapter, Encyclopedia of Energy, Volume 3, pp. 267-281, Elsevier Academic Press, New York, 2004.
- **Hydrogen Production**, Gene Berry, Invited chapter, Encyclopedia of Energy, Volume 3, pp. 282-294, Elsevier Academic Press, New York, 2004.
- **The Case for Hydrogen in a Carbon Constrained World**, Gene D. Berry and Salvador M. Aceves, Invited discussion paper, ASME Journal of Energy Resources Technology, 2005.
- **Vehicular Storage of Hydrogen in Insulated Pressure Vessels**, Salvador M. Aceves, Gene D. Berry, Joel Martinez-Frias, Francisco Espinoza-Loza, Submitted to the International Journal of Hydrogen Energy, 2005.
- **Cryogenic Hydrogen Storage**, Gene Berry and Salvador Aceves, Invited paper for “Materials for the Hydrogen Economy,” CRC Press, 2005.
- **Liner Materials for Composite Tanks**, Andrew Weisberg, Invited paper for “Materials for the Hydrogen Economy,” CRC Press, 2005.

Publication in Refereed Proceedings

- **Development and Demonstration of Insulated Pressure Vessels for Vehicular Hydrogen Storage**, Salvador M. Aceves, Gene D. Berry, Proceedings of the 15th World Hydrogen Energy Conference, Yokohama, Japan, June 27-July 2, 2004.

Technical Report

- **Hydrogen Absorption in Fluids: An Unexplored Solution for Onboard Hydrogen Storage**, Gene D. Berry, Lawrence Livermore National Laboratory Report UCRL-TR-209650, Livermore, CA, February 2005.
- **Proposed Standards for Hydrogen and Liquefied Natural Gas Insulated Pressure Vessels**, Report to the South Coast Air Quality Management District August 2004

Presentations

- **Advanced Hydrogen Containers**, Andrew Weisberg, Invited presentation, American Physical Society, March 2005.
- **Cryogenic Hydrogen Storage**, Salvador Aceves, Invited Presentation, Materials for the Hydrogen Economy, September 2005

Hydrogen Safety



The most significant hydrogen hazard associated with this project is:

- **Gigajoules of chemical energy released in the chaos of a vehicle crash**
- **Benchmark is 1 gigajoule = 278 kWh (lower heating value) of 8.33 kg of hydrogen stored on a vehicle**
- **Chemical energy sufficient to drive 300 miles dwarfs the mechanical energy in compressed fluids or in strained solids (several megajoules of 'spring' energy are stored in a 10,000 psi pressure vessel of automotive size)**
- **Roughly 5% of motor vehicle accidents result in a fire, all of these penetrate fuel storage, and these accidents are much more lethal (NTSB expert 2002)**

Approach to Safety



- Develop containers able to keep their contents inside despite significant impact and deformation
- Develop failure localization features that fail first when hydrogen pressure increases due to a crash
- Work on cryogenic containment of hydrogen or hydrogen materials, which has lower mechanical energy than ambient temperature or hot storage
- Work on liquid nitrogen absorption medium for reduced mechanical energy and reduced possibility of combustion in contact with air
- Demonstrate fast disposal through nozzles that mix released hydrogen with surrounding air to concentrations below the explosive and flammable limits without the possibility of combustion
- Avoid the possibility of combustion using the temperature drop of sonic nozzles and flow velocities above the flame speed of hydrogen+air
- Develop safety standards for cryo-compressed pressure vessels
- Build these nozzles in a slit-shaped form that can be realized in the post-rupture shape of a failure localization feature
- Demonstrate slow disposal through catalytic venting
- Convince those capable of volunteering for regulatory activities to re-word ISO TC197 so that hydrogen released within a container subassembly and mixed with air below the ignition limit or converted to water vapor is considered safe